



## **Zwitterionic Electroactive Polymer Actuators**

F49620-99-C-0073



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Physical Sciences, Inc.

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Air Force Office of Scientific Research  
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## REPORT DOCUMENTATION PAGE

AFRL-SR-AR-TR-02-

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

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1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE May 15, 2002		3. REPORT TYPE AND DATES COVERED Base Program Final Report, covering the period from 10/99 to 12/01	
4. TITLE AND SUBTITLE  Zwitterionic Electroactive Polymer Actuators				5. FUNDING NUMBERS  F49620-99-C-0073  J019-00 J019-02 62712E	
6. AUTHOR(S)  Mitchell R. Zakin, Susan T. Pasco, Amy B. Baldwin, Alan H. Gelb, John C. Magill, and Everett B. Anderson				8. PERFORMING ORGANIZATION REPORT NUMBER  PSI-1321/TR-1793	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)  Physical Sciences Inc. 20 New England Business Center Andover, MA 01810				10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)  USAF, AFMC 801 N. Randolph St, Rm 732 Arlington, VA 22203-1977				11. SUPPLEMENTARY NOTES	
12a. DISTRIBUTION AVAILABILITY STATEMENT  Distribution Statement A: Approved for public release; distribution is unlimited.				12b. DISTRIBUTION CODE  A	
13. ABSTRACT (Maximum 200 words)  Physical Sciences Inc. has developed an electroactive polymer-based material that undergoes a reversible conformational transition upon electrochemical reduction/oxidation. The enabling technology is a zwitterionic polyaniline derivative in which generation of +/- charge pairs upon oxidation provides significant conformational distortion along the polymer backbone, and a concomitant change in free volume. This novel actuation mechanism, analogous to that observed in lightly-crosslinked sulfonate gels, was confirmed using circular dichroism spectroscopy of thin supported polymer films. Despite our success in proving the validity of this novel actuation mechanism, the mechanical properties of zwitterionic polyanilines were not suited to the fabrication of polymeric actuators. Molecular mechanics calculations indicated that it may be possible to extended the zwitterionic actuation mechanism to other classes of electroactive polymers. This conjecture will be tested in the Option 1 portion of our proposed effort.					
14. SUBJECT TERMS				15. NUMBER OF PAGES 51	
				16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT  Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE  Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT  Unclassified	20. LIMITATION OF ABSTRACT		

## **1. BASE PROGRAM FINAL REPORT**

The project objectives, work carried out, results obtained, and estimates of technical feasibility are described in the charts attached as an appendix, presented at the Final Base Program Technical Review held at Physical Sciences Inc. (PSI) on 31 August 2000. DARPA attendees included Dr. Steve Wax, Mr. Randy Sands, Dr. Len Buckley (NRL), and Dr. Charles Lee (AFOSR).

## **2. PERSONNEL**

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## **3. PUBLICATIONS**

None.

# ***APPENDIX***

## **Zwitterionic Electroactive Polymer Actuators**

Physical Sciences Inc.

Base Program Final Report

Contract Number F49620-99-C-0073

# Objective and Technical Approach

## Objective

- Develop high-bandwidth, rugged, dry polymeric actuators using an electrostatic-driven mechanism for enhancing conformational changes in polymer structure

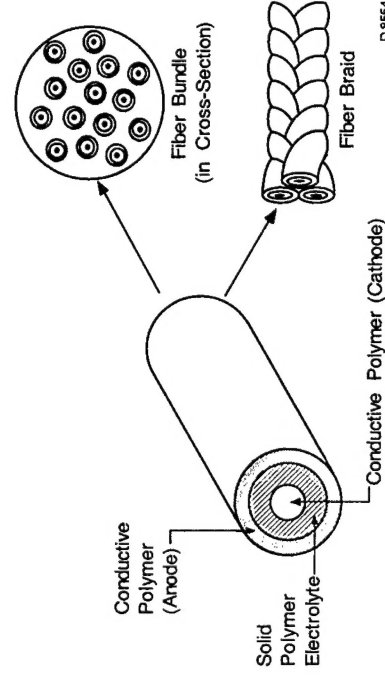
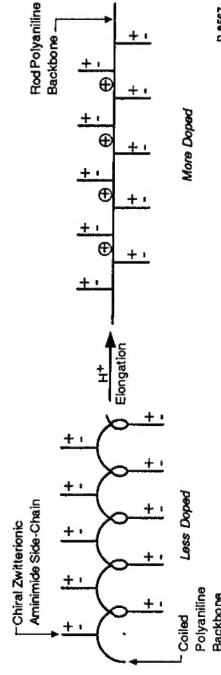
## Approach

- Coiled zwitterionic electroactive polymers maximize elongation/contraction for small changes in doping level
- Proton-doping increases speed, eliminates degradative negative counterion transport effects
- Muscle actuation using hydrated solid polymeric ionic conductors including Nafion
- Minimization of device power requirements by minimization of dopant transfer
- Fiber actuator design to "focus" elongation along a single linear dimension

## Milestones

- Demonstrate electrostatic "coil-rod" mechanism
- Demonstrate chemical control of actuation mechanism
- Estimate actuator performance

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# **Key Results**

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- **Were not able to synthesize aminimide-based polyanilines**
- **Demonstrated redox-driven conformational changes for three *self-doped* polyanilines**
  - self-doped polyanilines exhibit greater electrostatic effects and are easier to synthesize
- **Constructed and tested bender actuators – no actuation observed**
- **Modeled actuator performance and quantified workable ranges for desired material properties**
  - present self-doped polymers lack key properties required for actuator
- **Extended actuator concept to self-doped polythiophenes, which have key advantages over polyanilines**



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# Why Couldn't We Make Aminimide Polyanilines? - 1

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Synthesis and purification of desired monomers proved problematic

- Need ***electron-donating*** aminimides to promote aniline polymerization

- Common easy-to-make aminimides are electron-withdrawing (carbonyls)
- Well-established one-pot reaction is ineffective for synthesis of electron-donating aminimides
  - low yields
  - products difficult to purify
- Range of applicability of one-pot reaction is much narrower than expected
  - difficult to synthesize desired aminimide variants
  - steric hindrance, electronic effects are strongly deactivating

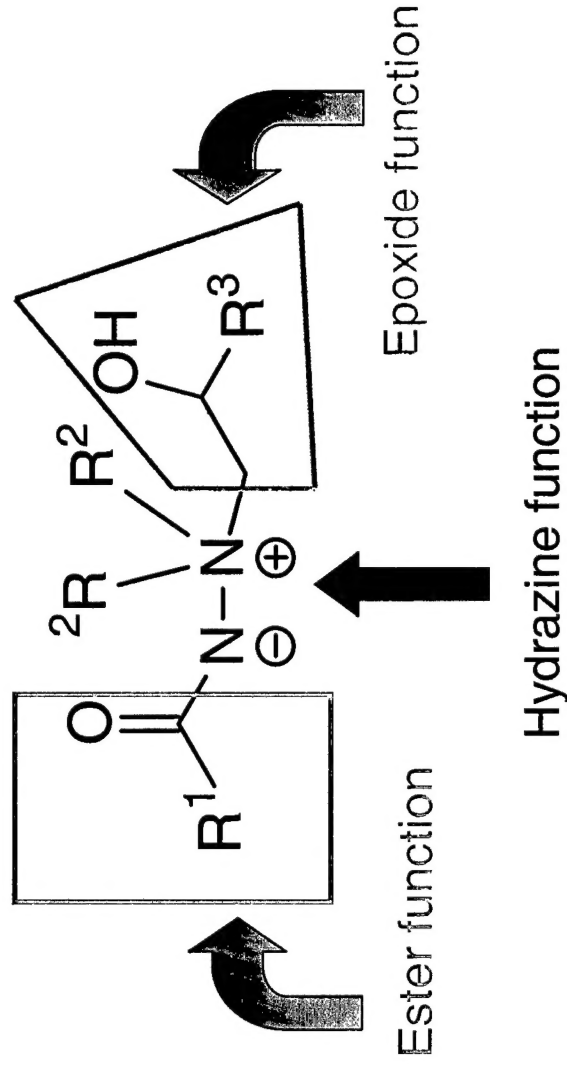
- **Electron-donating aminimides were not prepared in sufficient quantity or quality for polymerization**



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# Anatomy of an Aminimide

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- Aminimide properties are controlled through variation of the three basic functionalities
- Polymerizable aniline group can be placed on either end ( $R^1$  or  $R^3$ )

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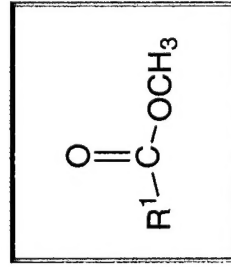


# Aminimide Synthesis

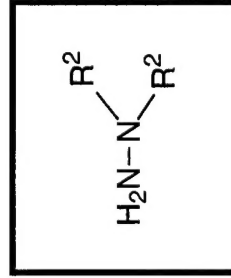
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- **Best route is simple *one-pot reaction* for aminimide synthesis**

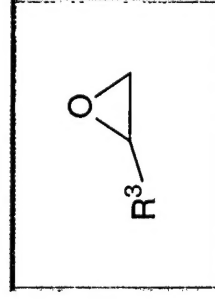
- mix ester, epoxide, 1,1-disubstituted hydrazine in alcohol
- stand at room temperature for ~3 days
- evaporate solvent, recrystallize from ethyl acetate, dry under vacuum
- yield ~ 50-60%



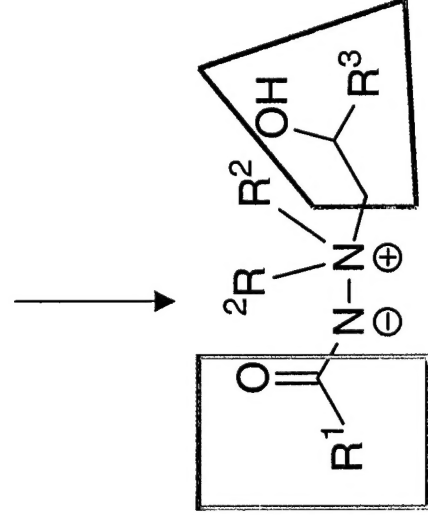
Ester



Hydrazine

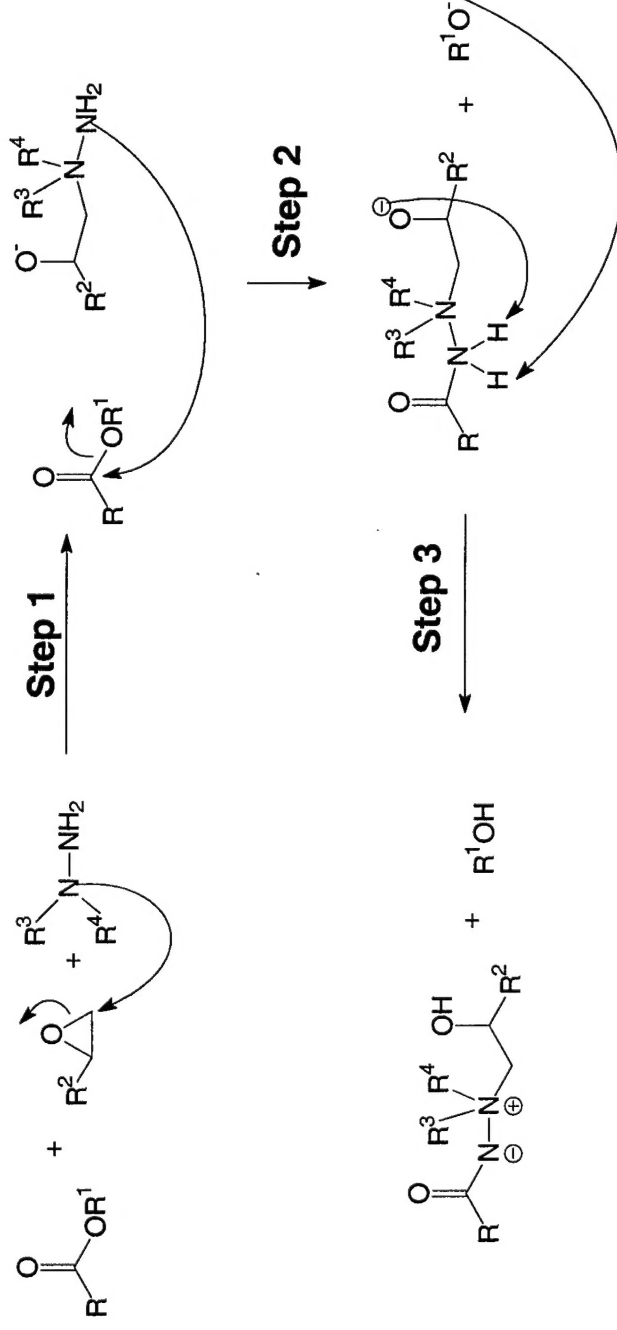


Epoxide



# Mechanism of One-pot Aminimide Synthesis

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**Step 1:** More electron-rich nitrogen on hydrazine attacks less-substituted side of epoxide.  
Epoxide opens up.

**Step 2:** Remaining nitrogen attacks ester. Alkoxide is ejected from ester.

**Step 3:** Both alkoxides deprotonate nitrogen.

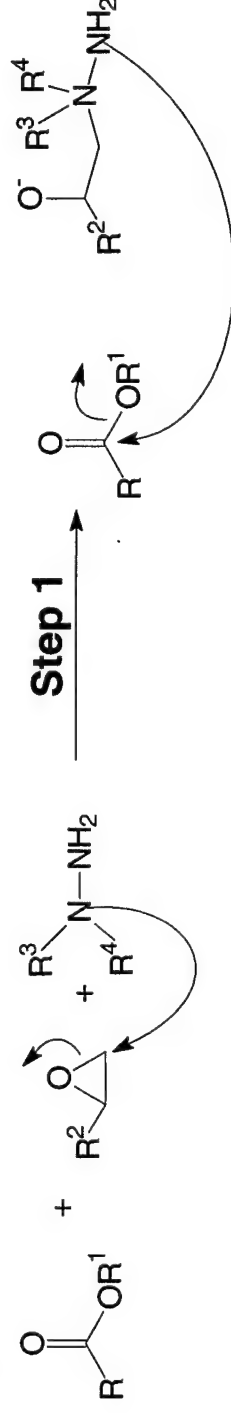
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# What Causes the One-pot Reaction to Fail? - 1

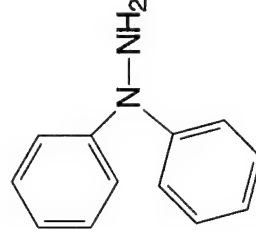
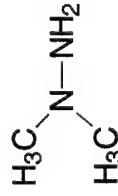
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- In Step 1:



If R<sup>3</sup> and R<sup>4</sup> are bulky, then attack at the epoxide is sterically hindered

Example:



Dimethyl hydrazine reacts, while diphenyl hydrazine does not.

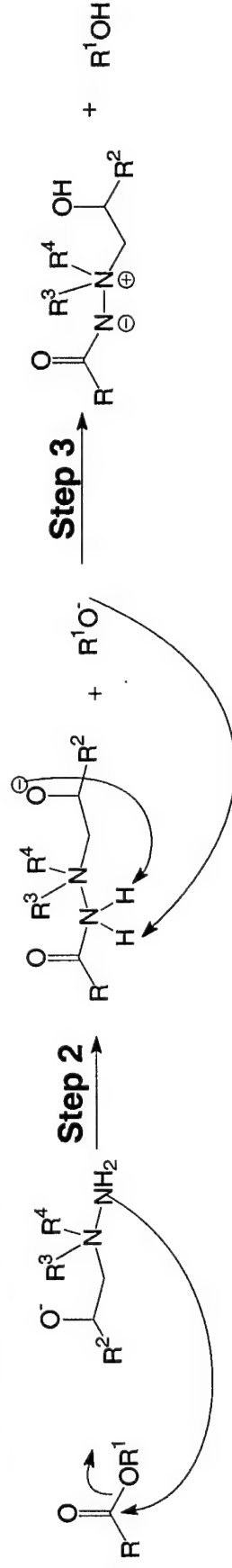
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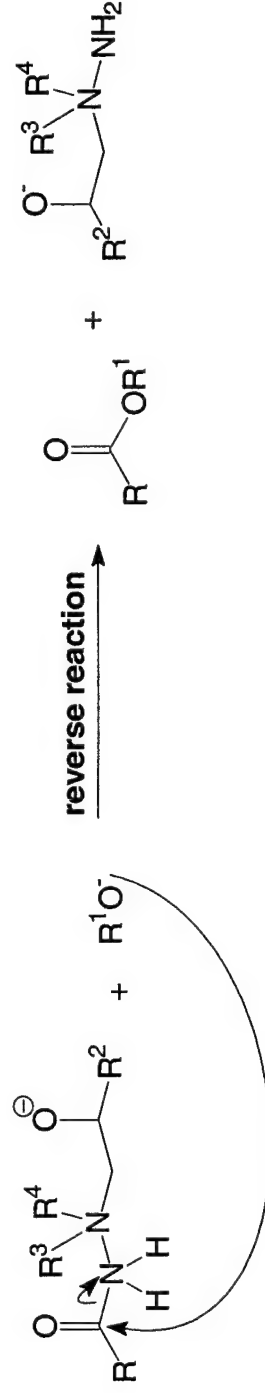
# What Causes the One-pot Reaction to Fail? - 2

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## • In steps 2 and 3:



When nitrogen attacks epoxide, deprotonation must occur faster than the reverse reaction:



If R can delocalize charge, then the product is stabilized and the forward reaction is favored. R groups such as phenyl facilitate the forward reaction.

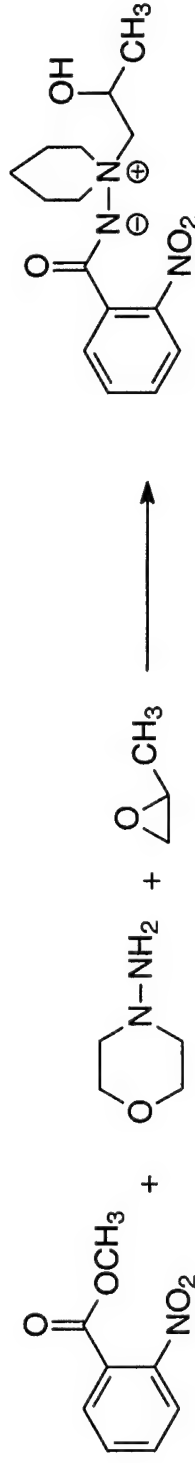
*R groups required to synthesize electron-donating aminimide-based aniline monomers cannot delocalize charge sufficiently to drive reaction.*

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# Synthesis of Typical Electron-Withdrawing Aminimide Monomer

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- Reaction was run on a 15 millimole scale
- Purified by recrystallization from ethyl acetate
- Product yield was ~30%

**This reaction was successful because the hydrazine is not too bulky and because the negative charge on the final product can be delocalized.**

**Yield was moderate because the hydrazine derivative is somewhat bulky and because some product is lost in the purification process.**

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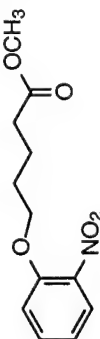
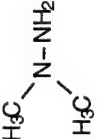
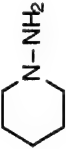
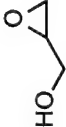
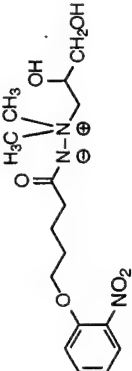
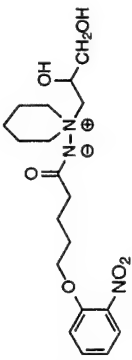

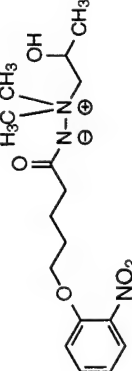
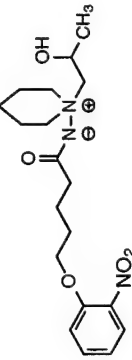
# Attempted Syntheses of Electron-Donating Aminimide Monomers - 1

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- Short-chain ester reactant cannot delocalize charge on nitrogen; thus reaction is hindered
- Bulky morpholino hydrazines further slow down reaction
- HPLC of crude product mixture shows 3-15 peaks, indicating incomplete reaction sequence and/or multiple mechanistic pathways
- Literature suggests *one* pathway
- All reactions have a common unknown side-product

# Attempted Syntheses of Electron-Donating Aminimide Monomers - 2

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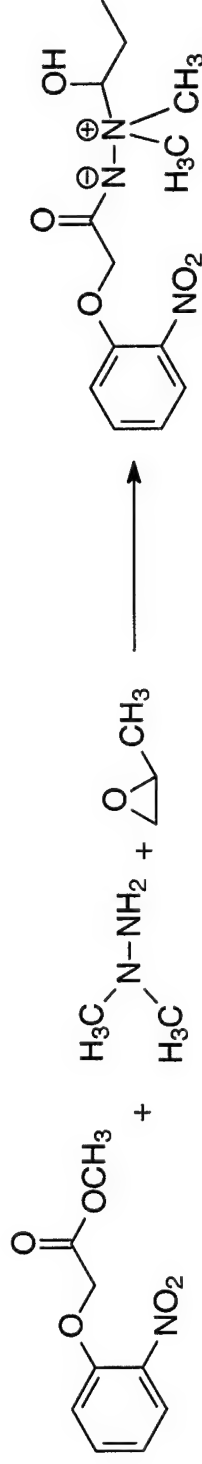
- Longer-chain ester reactant
- Results qualitatively similar to short-chain ester, but with lower product yield
- HPLC analysis indicates that glycidol produces the most side-products, perhaps due to a competing trans-esterification reaction
- All products have a common unknown side-product

# Purification of Aminimides from Crude Reaction Mixture

VG02-124-12

HPLC and TLC indicate that there are typically 3-15 products and starting materials in reaction mixture

- Low-boiling starting materials can be removed by vacuum
- Recrystallizations from ethyl acetate or *iso*-propanol were unsuccessful
- Chromatography could not separate products



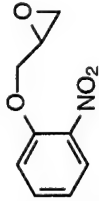
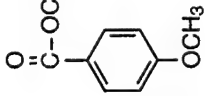
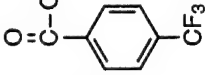
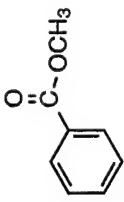
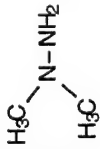
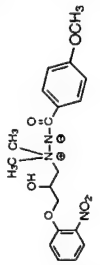
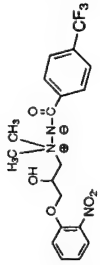
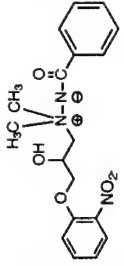
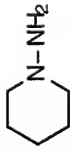
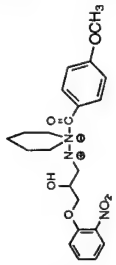
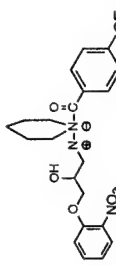
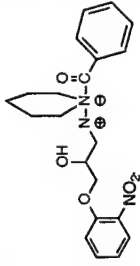
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# Attempted Syntheses of Electron-Donating Aminimide Monomers - 3

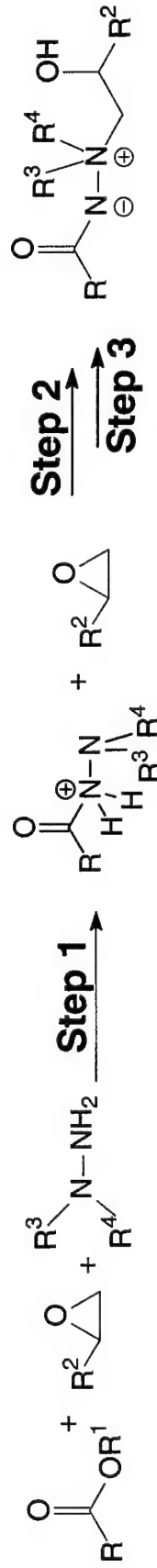
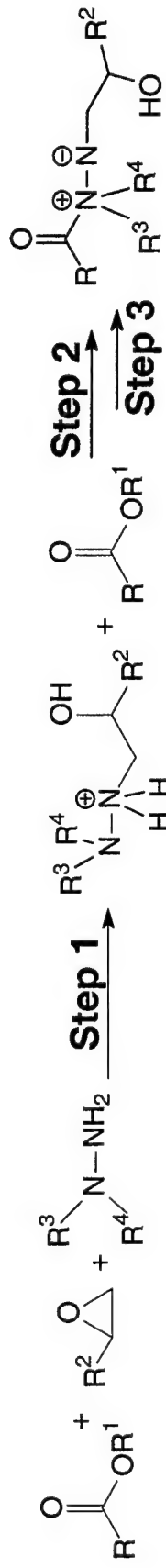
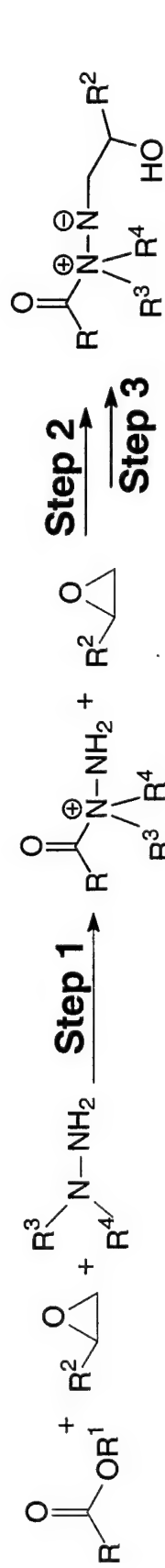
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- Epoxide reactant designed to place aniline on opposite end of aminimide moiety
- Reactions "should" work, since esters can delocalize charge
- All reactions yielded at least 6 products according to HPLC analysis
- Results indicative of multiple partially completed mechanistic pathways

# Alternate Aminimide Mechanistic Pathways

VG02-124-14



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# ***Why Couldn't We Make Aminimide Polyanilines? - 2***

VG02-124-15

**Attempts to polymerize electron-*withdrawing* aminimide monomers proved unsuccessful**

- **Steric hindrance of bulky aminimide moiety severely inhibits polymerization**

- reduces polymerization rate
- lowers MW due to higher probability of chain termination

- **Electron-withdrawing substituent on aniline ring inhibits oxidation at p-position required for chain propagation**

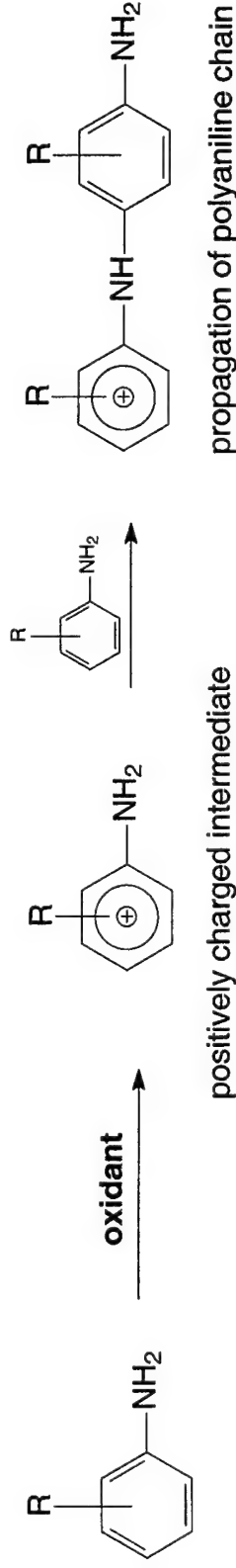
- **Direct conversion of polyaniline esters to aminimides via the one-pot reaction not feasible due to low polymer purity**



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# Polymerization of Substituted Anilines

VG02-124-16



## Electronics are important:

- Polymerization proceeds via a positively charged intermediate
- If **R** is electron-withdrawing, then intermediate is destabilized
- If **R** is electron-donating, then intermediate is stabilized
- Destabilization of intermediate leads to **chain termination**
- Position that is *para* to the  $\text{NH}_2$  is most activated  $\Rightarrow$  polyaniline is all *para*-linked

## Sterics are also important:

- If **R** is *ortho* to  $\text{NH}_2$  then reaction proceeds faster than if **R** is *meta*
- Reaction is fastest if **R** is H

**Electron-withdrawing aminimide-substituted anilines do not polymerize!!!**

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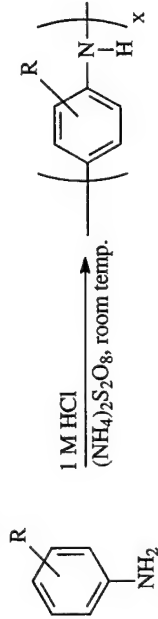
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# Methodology for Polymerization of Substituted Anilines

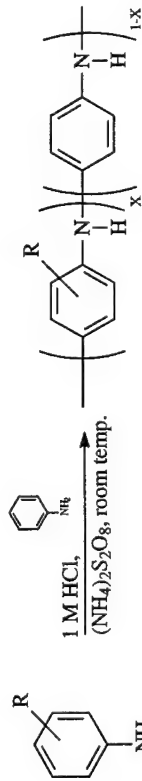
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Three primary methods – all use  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  as oxidant

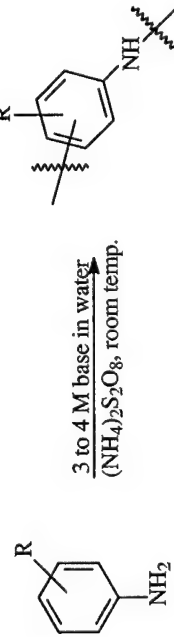
## 1. Acidic conditions



## 2. Copolymerization with aniline under acidic conditions



## 3. Basic conditions

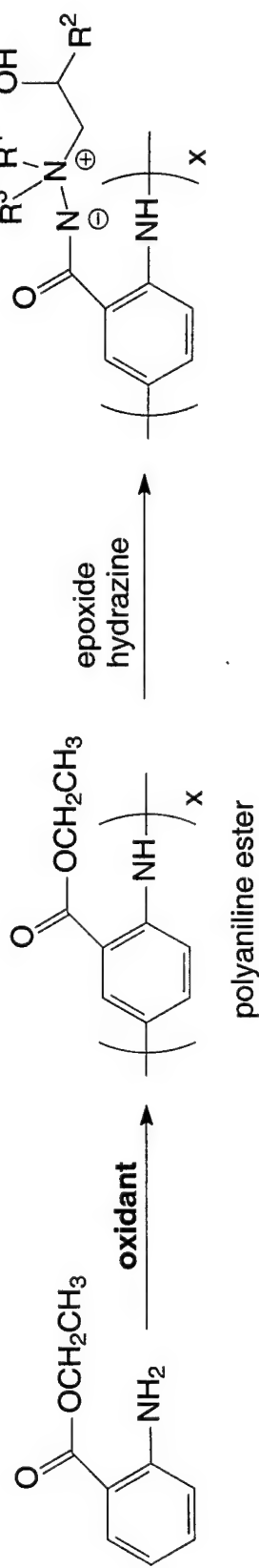


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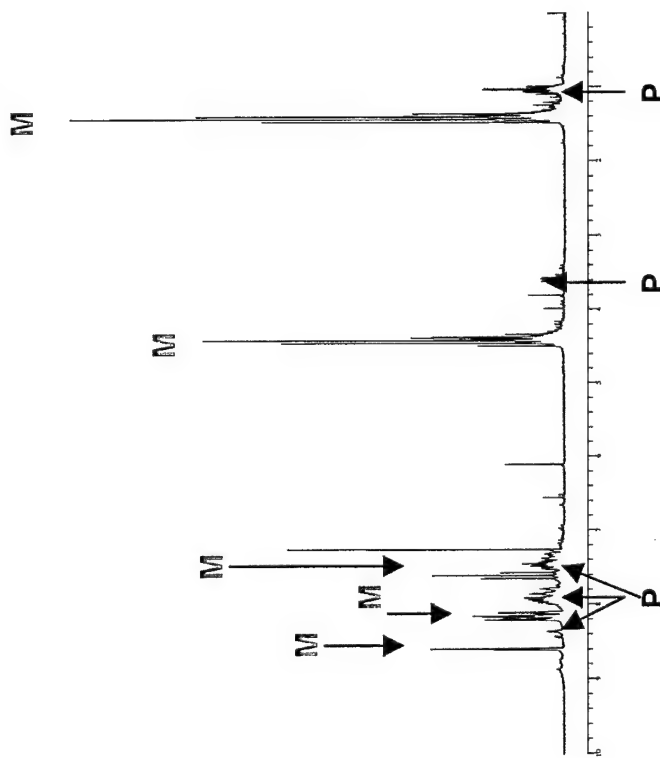
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# Alternate Synthesis of Aminimide Polyanilines

VG02-124-18



**Polymerization of ester failed due to electron-withdrawing effect on aniline**  
 — yield is 1.3% after 24 hr reaction, but consists mostly of monomer or short oligomer



sample #8, poly(ethyl-3-aminobenzonate)

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# ***Aminimide-Based Polyanilines - Conclusions***

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VG02-124-19

- We never produced aminimide polyanilines
- Aminimide-based actuators could not be constructed and characterized
- Feasibility of proposed actuation concept could not be evaluated



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# ***Rationale for Self-Doped Polymers as Actuators***

VG02-124-20

- **Actuation mechanism analogous to aminimide polyanilines**
- **Stronger electrostatic interactions should generate enhanced conformational distortion (ion-ion versus ion-dipole)**
- **Synthesis of self-doped polymers is more tractable**

<b>Advantages</b>	<b>Disadvantages</b>
More facile synthetic procedures	May be water-soluble
Processible from organic solvents	Mechanical properties largely unknown
Strong redox-reversible electrostatic forces	Films hard to cast, can be brittle
Compatible with broad range of electrolytes	Lower electrical conductivity than polyaniline
Fixed dopant counterions may increase actuation speed	Redox characteristics largely unknown



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# Actuation Mechanism for Self-Doped EA Polymers

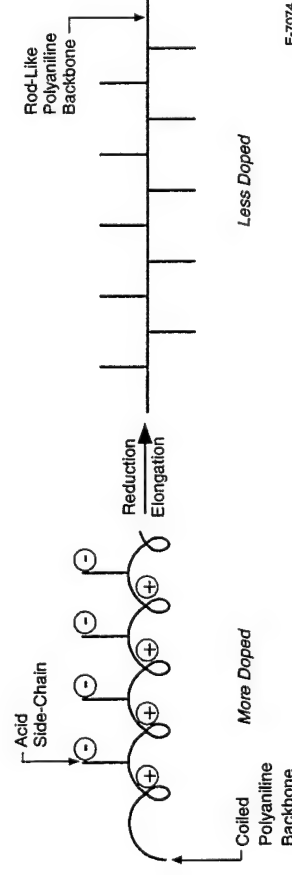
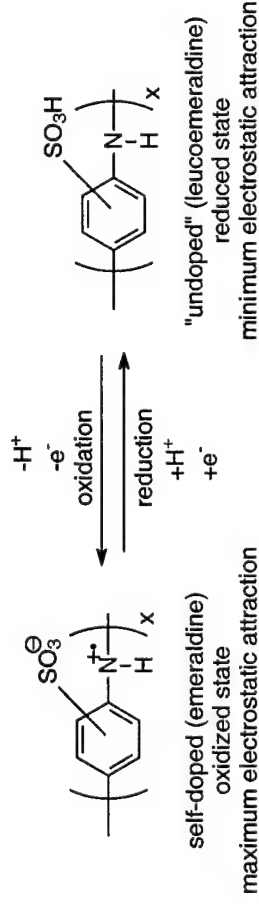
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**Strong acid groups (-SO<sub>3</sub>H) dope polymer; negative counterions remain fixed to polymer backbone**

- doping creates charge separation
- redox processes cannot uptake/expel counterions
- reversible electrostatic interaction between negatively charged side-chain and + backbone upon redox provides reversible conformational distortion

**Lack of counterion diffusion should increase actuation speed (rate-limiting step)**

**Prototypical self-doped EA polymer is SPAN (sulfonated polyaniline)**



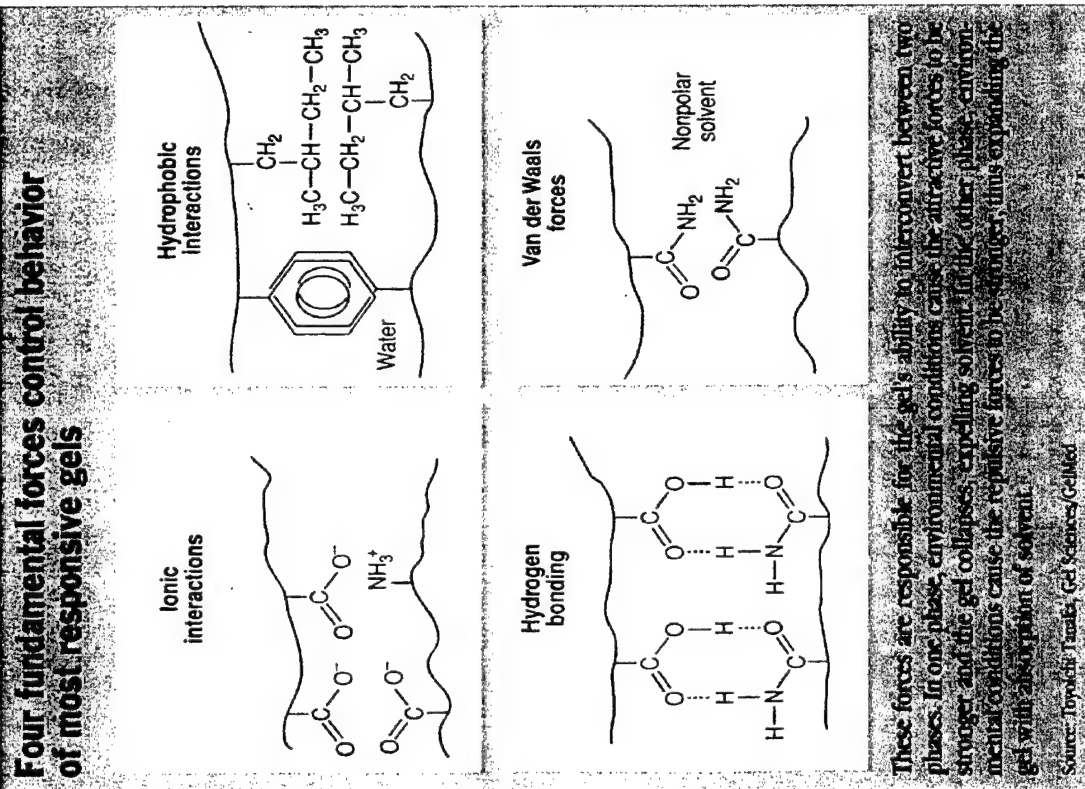
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# Self-doped EA Polymers Resemble Responsive Gels

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# ***How Do We Expect Self-Doped Polymers to Perform?***

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- **Self-doped polymers should exhibit a strong transition from a tightly coiled form in the oxidized (ionized) state to a less coiled form in the reduced (neutral) state**
  - the coiling-uncoiling transition will produce a significant redox-reversible change in polymer dimension (e.g., volume)
- **Linear bending actuators constructed from self-doped polymers will exhibit greater actuation, generated by proton transport, than identical “baseline” polyaniline actuators**



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# ***Proof-of-Concept Experiments Performed***

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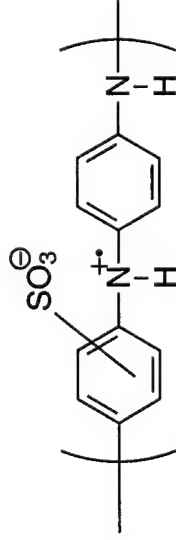
- Synthesized three self-doped polyanilines with different structural and electronic characteristics
- Fabricated thin polymer films for conformational analysis
- Characterized redox-induced coiling-uncoiling transition using circular dichroism (CD) spectroscopy
- Performed molecular mechanics calculations of polymer coiling and compared to CD results
- Built and characterized linear bending actuators from self-doped polymers



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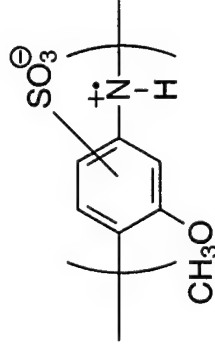
# Characteristics of Self-Doped Polyanilines

VG02-124-25



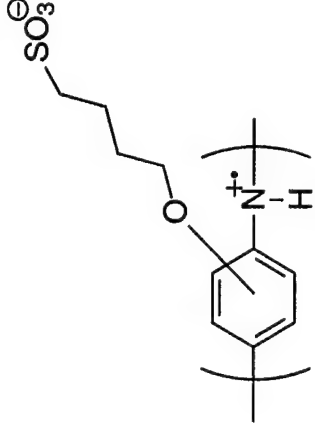
**ZPani**

- SO<sub>3</sub><sup>-</sup> on alternate monomer units



**ZPani-activated**

- SO<sub>3</sub><sup>-</sup> on every monomer unit
- electron-donating -OCH<sub>3</sub> delocalizes + charge
- higher conductivity



**ZPani-spacer**

- SO<sub>3</sub><sup>-</sup> on every monomer unit
- increased distance between SO<sub>3</sub><sup>-</sup> and + charge
- lower conductivity

# Synthesis and Properties of Self-Doped Polyanilines

VG02-124-26

Polymer	ZPani	ZPani - activated	ZPani - spacer
Conductivity	$10^{-4}$ S/cm; 0.01 S/cm	0.1 S/cm	0.005 S/cm
$M_w$ (GPC vs. polystyrene std)	10,000; 84,000 Daltons	10,400 Daltons	10,000 Daltons (est)
Polydispersity	4	1.42	---
Solubility	DMSO, NMP/ $\text{NEt}_3$	Water, DMSO	Water, DMSO
Monomer substituent properties	Strongly electron-withdrawing	Both e-withdrawing and donating; meta and para linkages possible	Electron-donating
Polymerization Method	Sulfonation of PAni with fuming sulfuric acid	Oxidative under basic conditions	Oxidative under acidic conditions

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# ***Polymer Conformational Analysis by CD Spectroscopy***

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VG02-124-27

- **Circular dichroism (CD) spectroscopy is the only practical method for solid-state polymer conformational analysis**
  - CD signal (ellipticity) is difference in absorbance of right- and left-circularly polarized light by structural features (coils)
  - CD signals arise only at (strong) polymer absorption bands
  - most sensitive to asymmetric (i.e., chiral) conformations
  - technique demonstrated for polyanilines by MacDiarmid and Wallace
- **CD spectrum measures handedness (+ or -) and *relative* abundance of conformational features**
  - best for comparison of changes in coiling due to redox, chiral processing, etc.
- **Relevant polyaniline spectral absorption features occur in the visible region**

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# ***Experimental Procedure for Conformational Analysis***

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- **Synthesize self-doped polyaniline**
- **Fabricate polymer thin-film from DMSO onto glass slide by casting**
- **Obtain UV-Vis spectrum to confirm oxidation state**
- **Measure CD spectrum to determine polymer coiling**
- **Switch polymer oxidation state (emeraldine to leucoemeraldine) using chemical means**
  - soak polymer film in solution of oxidizer (m-chloroperoxybenzoic acid) or reducing agent (hydrazine) in isopropanol
- **Measure CD spectrum to determine redox-induced change in coiling**

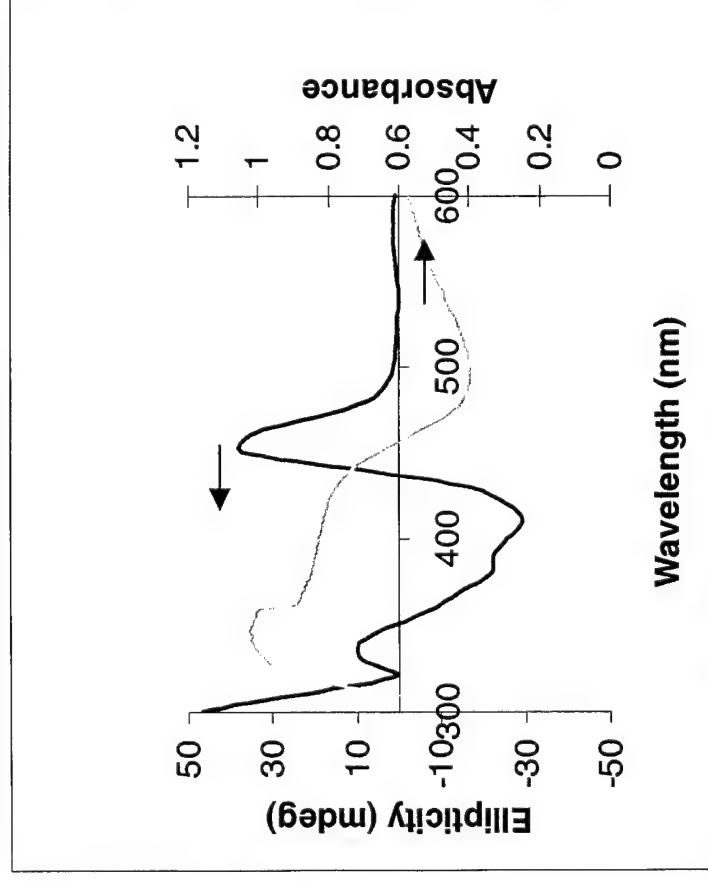


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# CD Spectrum of Chiral-Doped Polyaniline

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- Polyaniline does not exhibit native asymmetric backbone coiling (absence of CD spectrum)
- Doping with the chiral dopant camphorsulfonic acid (+CSA) introduces +chiral polymer conformation
- CD bands correlate with UV-Vis absorption features of emeraldine (oxidized) state

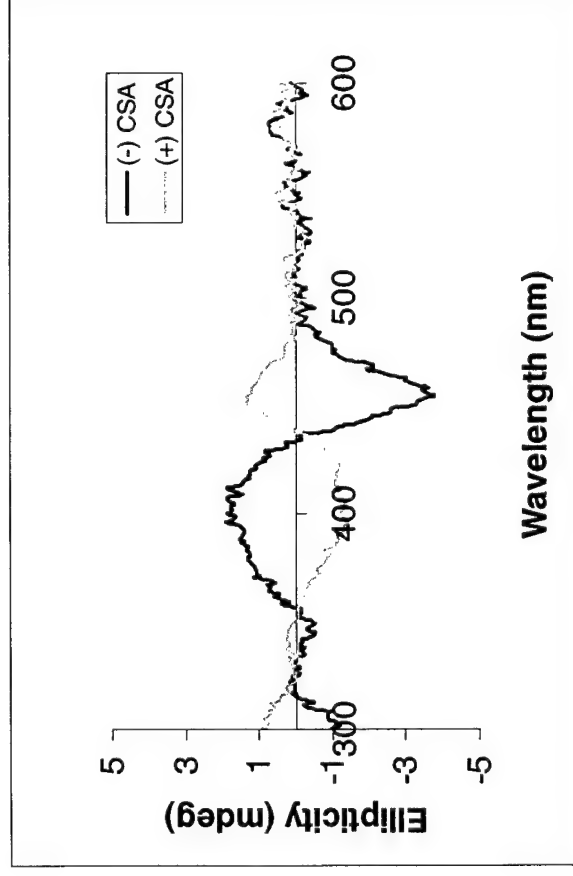
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# Chiral Processing Alters Polyaniline Chirality

VG02-124-30

- Generate mirror-image conformations of polyaniline backbone via incorporation of mirror-image dopants ( $\pm$ )CSA
- Initial polymer conformation can be “locked in” by chiral processing
- Coiling also affected by choice of solvent for film fabrication

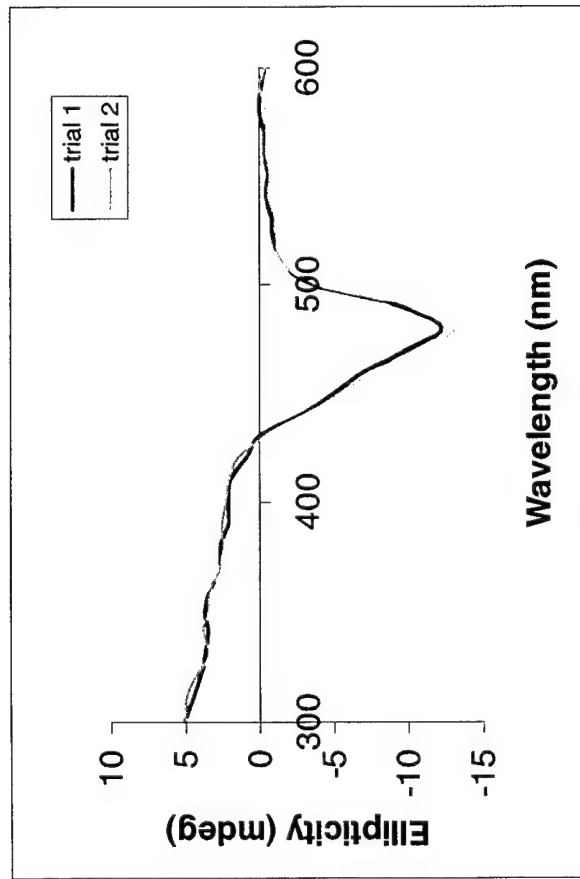


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# Reproducibility of CD Spectral Measurements

VG02-124-31

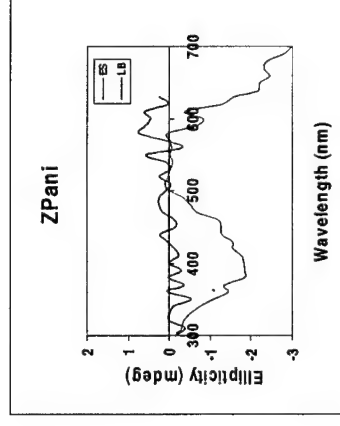


- ZPani-activated film in oxidized state
- Remove, re-insert film into Jasco J-710 spectropolarimeter

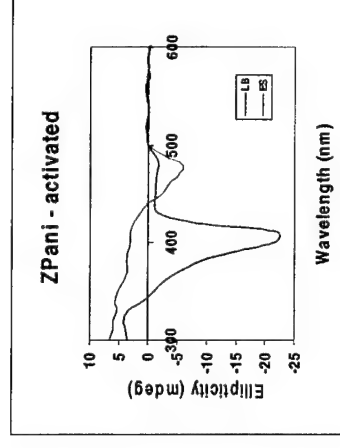
# Conformation of Self-Doped Polyanilines Depends on Oxidation State

VG02-124-32

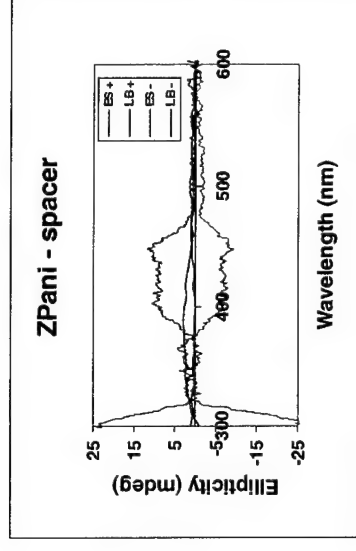
- Self-doped polyanilines exhibit different chiral backbone conformations in the oxidized (ES) and reduced (LB) forms
- Small structural and electronic differences produce striking changes in coiling/uncoiling behavior
- Simple “isolated polymer chain” electrostatics are in general agreement with, but not sufficient to explain, observed results
  - chain-chain electrostatic and steric coupling are key conformational drivers
- Close proximity of acid group to backbone appears to be required for native (intrinsic) asymmetric polymer coiling
- Polymer films craze/delaminate from substrate during redox, thus “actuate”



Native coiling; decreased upon reduction



Native coiling; enhanced upon reduction



Chirally processed coiling; decreased upon reduction

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# Molecular Mechanics of Electroactive Polyanilines

VG02-124-33

- **Performed configurational calculations using HyperChem commercial software package**
  - molecular mechanics with MM+ force field; allows charges
  - reduced and oxidized forms of isolated polymer chains
- **Self-doped polyanilines are more coiled than polyaniline**
- **Investigated effect of spacing between acid group and polymer backbone on conformation**
  - smaller spacing provides greater coiling in oxidized state, greater reduction in coiling in reduced state
  - ZPani exhibits largest coil-uncoil transition upon redox
  - ZPani-spacer exhibits greatest coiling in *half-oxidized* state
- **Calculations generally consistent with CD measurements**

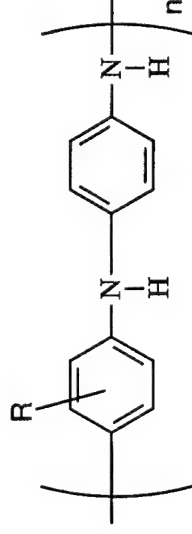
## Systems studied:

R = H (n=32) - *polyaniline*

R = SO<sub>3</sub>H (n=32) - *ZPani*

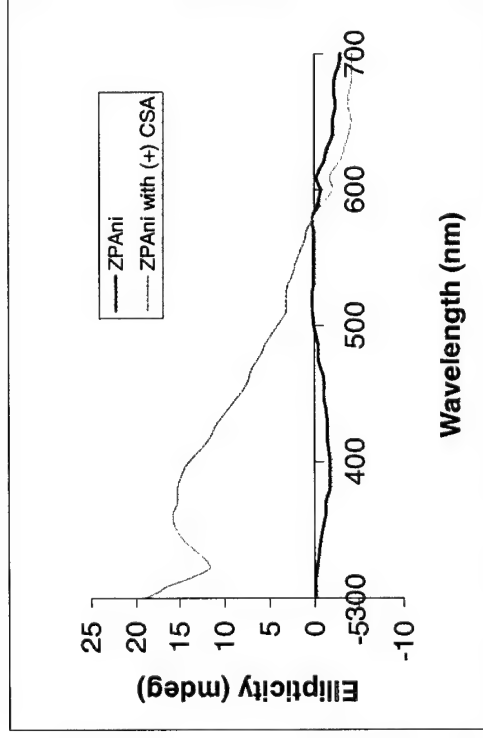
R = O(CH<sub>2</sub>)<sub>3</sub>SO<sub>3</sub>H (n=16) – “*ZPani-spacer*”

R = O(CH<sub>2</sub>)<sub>6</sub>SO<sub>3</sub>H (n=16)



# Chiral Processing Alters Self-Doped Polymers

VG02-124-34

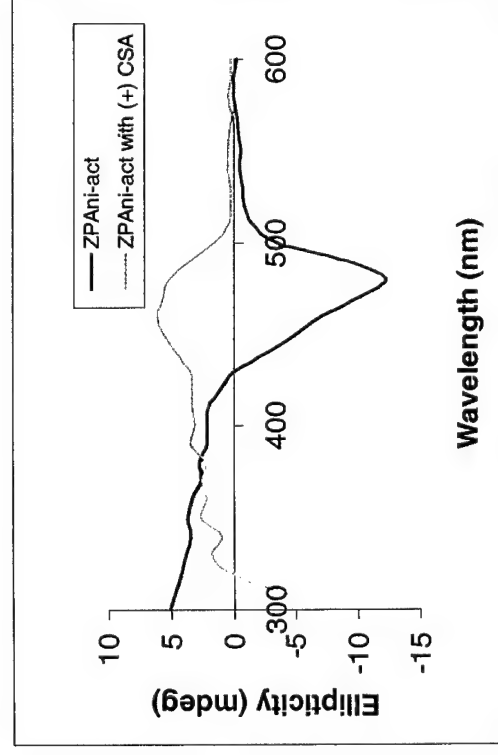


## Add (+) or (-)CSA to self-doped polymer in DMSO solution, cast film

- ZPA ni in oxidized state
- ZPA ni-activated in reduced state
- conductivity affected by CSA treatment?

## Chiral dopant forces polymer to change conformation of backbone (handedness)

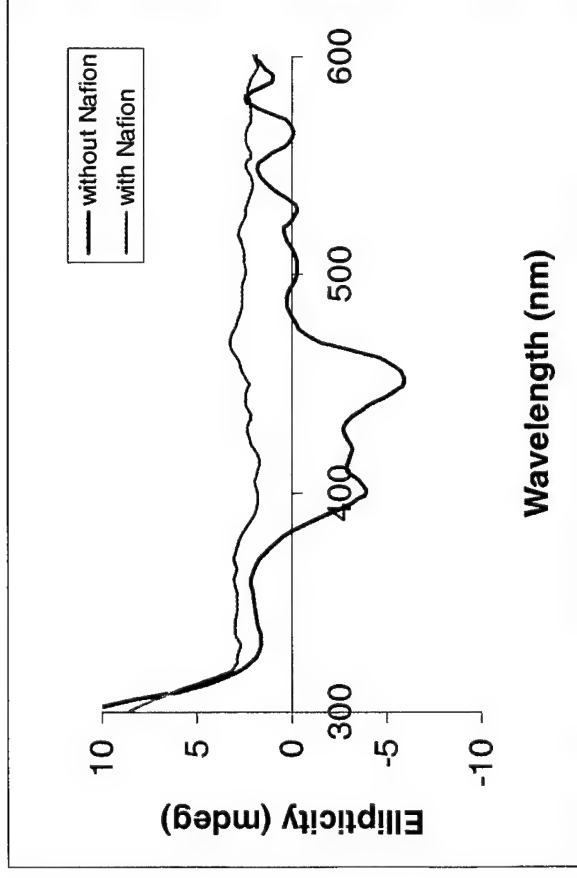
## Chiral processing alters conformation of both polyaniline and self-doped polyanilines



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# Effect of Nafion Electrolyte on Polymer Coiling

VG02-124-35



## • Blending of 30% (w/w) Nafion into ZPani-spacer with (+)CSA dopant reduces coiling

- Nafion is an acidic sulfonated fluoropolymer which acts as a large immobile dopant, holding ZPani backbone in place
- similar results observed for other ZPani self-doped polymers

## • Constrains actuator design to polymer-Nafion-polymer layered configuration



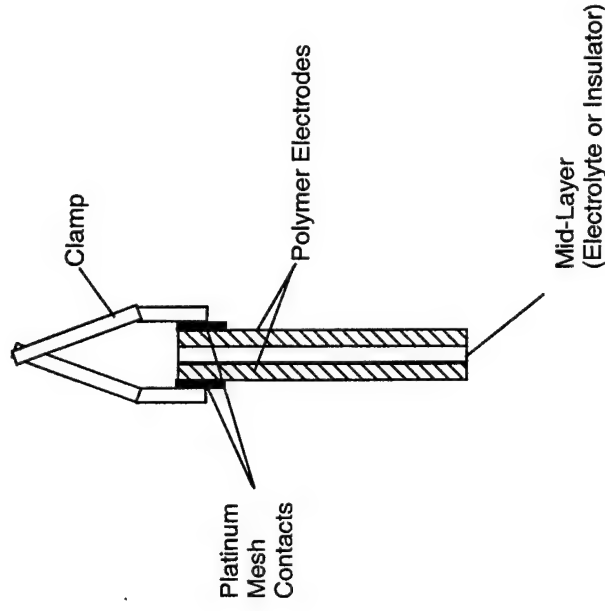
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# Construction and Testing of Polymer Actuators

VG02-124-36

- **Constructed simple bender actuators**
  - polymer-insulator and polymer-Nafion sandwich configurations
  - studied polyaniline and ZPani
- **Poor film quality and poor adhesion to Nafion hindered fabrication and characterization of proton-transfer actuators**
- **Actuation observed only for polyaniline in aqueous HCl electrolyte– ZPani did not bend**
  - Polyaniline conductivity 25-40 S/cm
  - ZPani conductivity ~ 0.01 S/cm

## Bender Construction



- **Three-layer construction bends due to differential strain in electrodes**

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# ***Bender Polymer Properties***

VG02-124-37

## **Polyaniline**

- conductivity 25-40 S/cm
- poor solubility in NMP and DMSO, but casts well from DMPU
- strong free-standing films possible
- good films were approximately 13  $\mu\text{m}$  thick

## **ZPani**

- conductivity ~ 0.01 S/cm hydrated
- various solvents and drying processes were tried, but best films were cast from NMP
- films have low tensile strength and are thus very fragile
  - limiting factor in actuator fabrication and testing
- films were approximately 5  $\mu\text{m}$  thick
- material is weakly water-soluble
- bonding to ZPani films is difficult

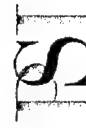


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# Material Test Matrix and Results

VG02-124-38

#	Electrode	Mid-Layer	Bath	Bending?
1	PANI	Tape	1M HCl	Yes
2	PANI w / Nafion Coat	Tape	1M HCl	No
3	PANI	Nafion	1M HCl	Yes
4	PANI	Nafion	Air	No
5	ZPani	Nafion	Air	No
6	ZPani	Platinized Nafion	DIUF	No
7	ZPani	Tape	1M HCl	No



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# ***Conclusions – Polyaniline Conformational Studies***

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VG02-124-39

- **The conformation of self-doped polyanilines depends on oxidation state**
- **Polymer coiling decreases as spacing between negatively-charged acid side-chain and positively-charged backbone increases**
- **Electron-donating groups appear to partially screen electrostatic interactions to reduce coiling in oxidized state**
- **Polymer chiral conformation can be altered by material processing**
- **Blending of Nafion into self-doped polyanilines reduces asymmetric coiling**
- **Not able to achieve actuation of self-doped polymers (due to insufficient conductivity)**



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# Conduction Model for Linear Actuators

VG02-124-40

- Redox reactions driven by local overpotential

$$\eta(x) = \eta(0) - V_{iR}(x)$$

- $i(x) = i_0 e^{\alpha \eta(x)}$  (Butler-Volmer equation);  $\alpha \sim 20 \text{ V}^{-1}$

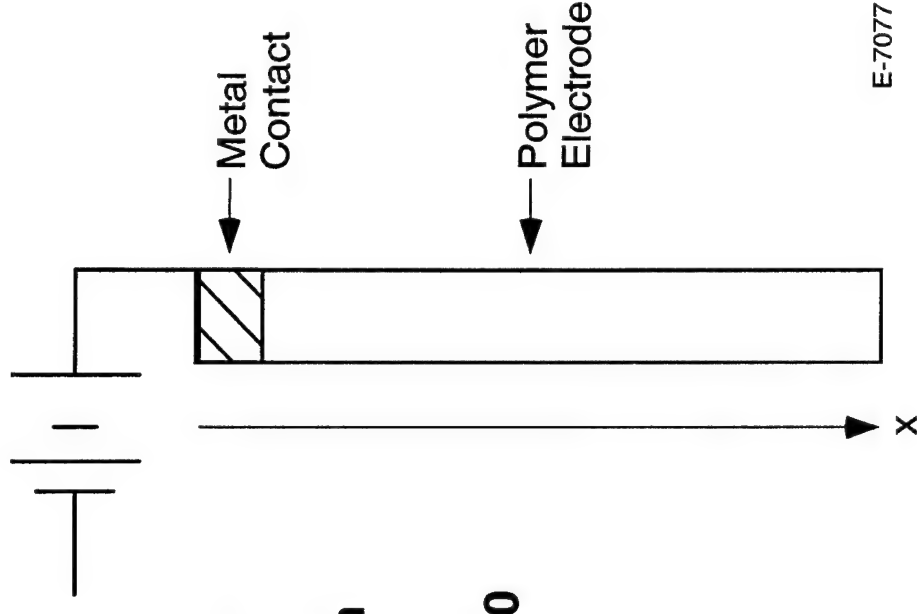
- Electrical conductivity must be sufficiently high so that  $V_{iR}(x)$  small

- $V_{iR}(x) \sim 0.1 \text{ V}$  decreases local rate by factor of 10 relative to  $V_{iR}(0)$  (contact point)

- Parameters for PANI-type electrodes

- $20 \mu\text{m}$  thick
- length =  $1 \text{ cm}$ , width =  $0.1 \text{ cm}$
- $Q = 100 \text{ mC}$
- switching time =  $1.0 \text{ second}$
- $\therefore$  total current =  $100 \text{ mA}$

- Conclusion: high conductivity required



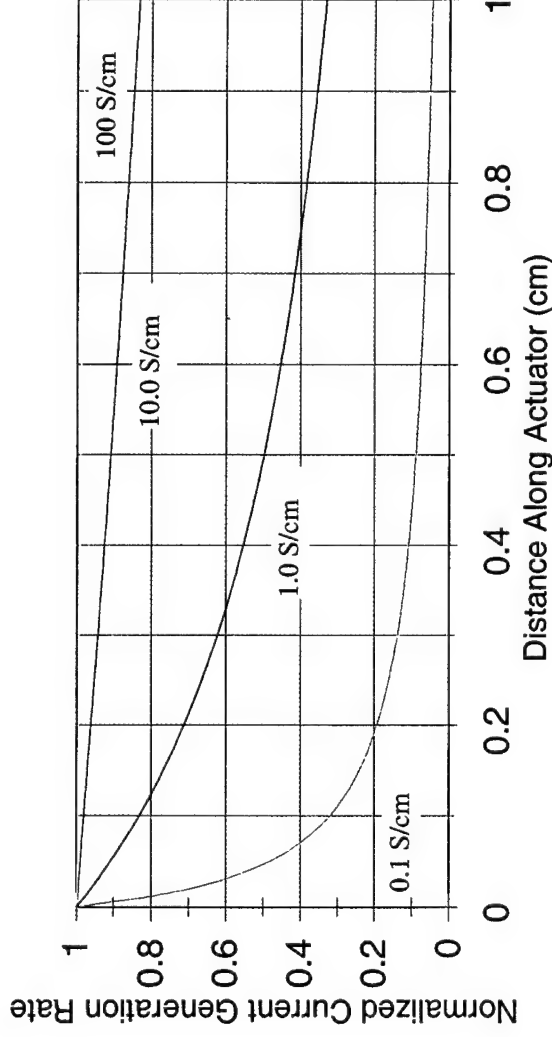
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# Variation of Current Along Linear Polymeric Actuator

VG02-124-41



## Current declines along length of polymer electrode due to resistive ( $iR$ ) losses

- effect greatest at lowest conductivities
- for modest actuator length (1 cm), effective actuation only achievable for  $\sigma \geq 10$  S/cm
- self-doped polyanilines presently have insufficient conductivity ( $< 0.01$  S/cm) to exhibit actuation

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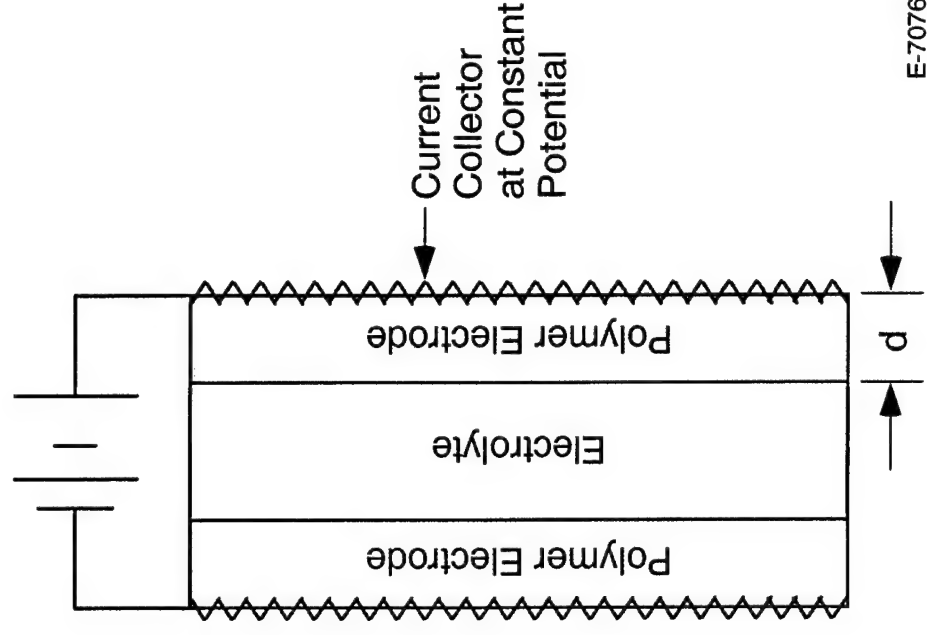
# Conductivity Model for Cell Actuators

VG02-124-42

- Polymer density  $\rho = 1 \text{ g/cc}$
- Electrode thickness  $d$
- Equivalence weight  $\omega_e = 200 \text{ amu}$
- Actuation time  $t$
- Current  $i$ , current density  $j$
- $j = F (\rho d / \omega_e) / t$  required for actuation
- $j \sim e^{\alpha(\eta - iR)}$  Butler-Volmer equation ( $\alpha \sim 20 \text{ V}^{-1}$ )
- Want efficient electrode redox:

$$j_{\min} / j_{\max} \sim 0.5 \Rightarrow \alpha(-iR) \sim 0.4$$

- Conclusion: 1 to 10 S/cm required

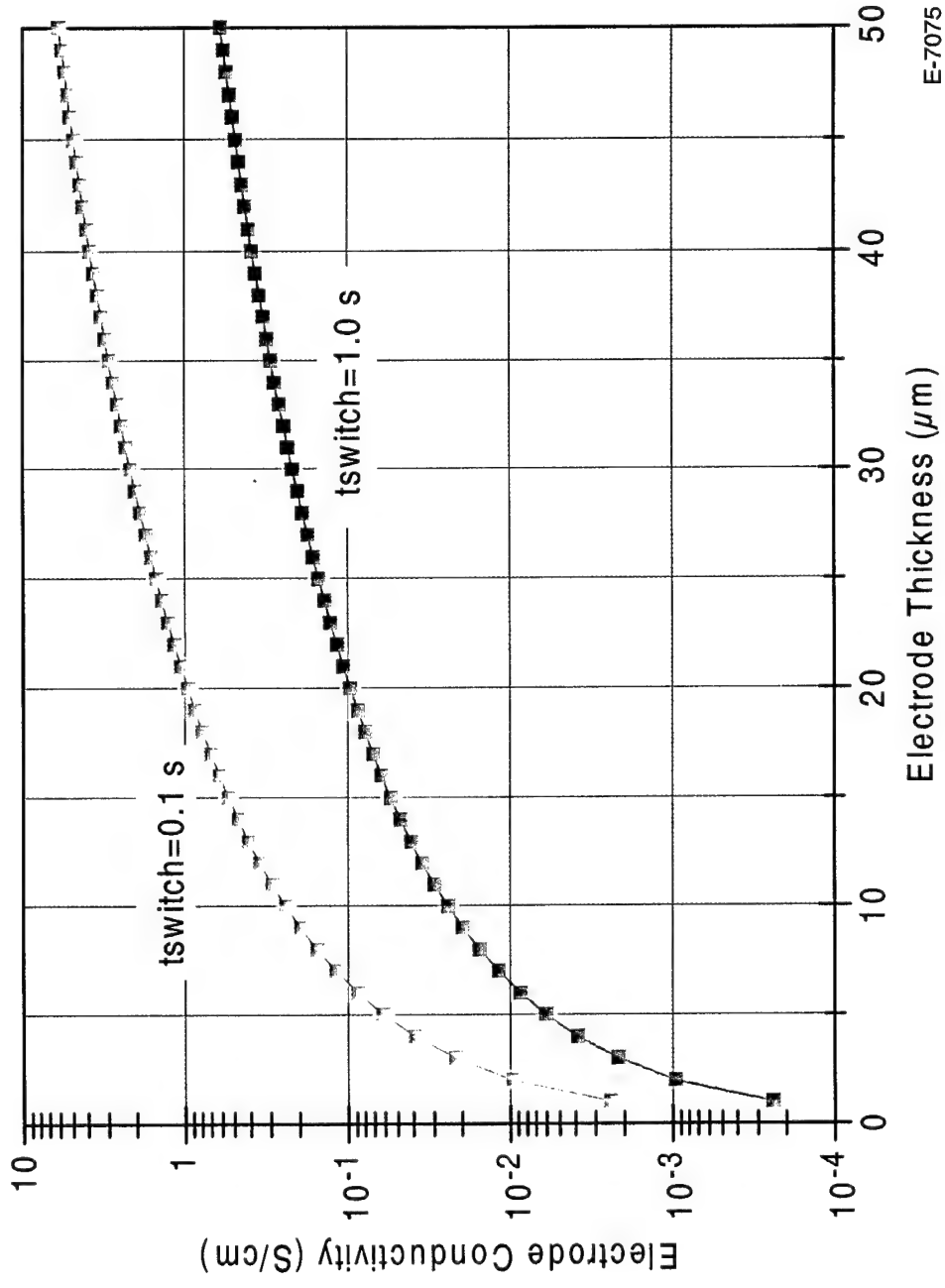


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# Polymer Conductivity Required for Efficient Redox

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# ***Desired Material Properties for Self-Doped Actuators***

VG02-124-44

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**Based on experiments and modeling, we conclude that the following minimum polymer characteristics are required for actuation:**

- **Conductivity  $\geq 10$  S/cm**
- **MW > 10,000 amu**
- **Insoluble in water**
- **Soluble in organic solvents**
- **Processible from organic solvents**



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# ***Concept Extension – Polythiophenes as Self-Doped Actuators***

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VG02-124-45

**Polythiophenes have several key advantages:**

- **High conductivity (regioregular versions  $\leq 1000$  S/cm)**
- **Simpler, more rapid polymerization**
  - works for monomers containing bulky side-groups
  - monomers harder to make, but significant literature exists (Reynolds)
- **Exhibit fast redox switching, long cycle lifetime in electrochromic cells (Reynolds)**
- **Strong chiral coiling observed for dibutoxy derivatives (Meijer)**
- **Simple two oxidation state system (unlike polyanilines)**
- **Self-doped versions have conductivities  $\sim 5 - 10$  S/cm (LeClerc)**
- **PSI has significant polythiophene experience for sensor applications**

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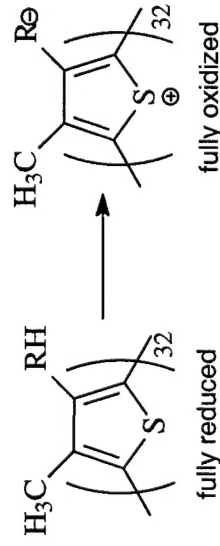
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# Molecular Mechanics of Self-Doped Polythiophenes

VG02-124-46

- Performed configurational calculations for representative self-doped polythiophenes as a function of oxidation state

—  $R = -O(CH_2)_2SO_3$ ,  $R = -(CH_2)_2SO_3$  (water-soluble)



- Calculations predict reduction of polymer “size” with progressive ionization of acid side-chains (oxidation)

Ionization State	End-to-End Distance (Å)	
	$R = -(CH_2)_2SO_3$	$R = -O(CH_2)_2SO_3$
Fully reduced	77	86
50% oxidized	24(l), 45(w)	24(l), 50(w)
Fully oxidized	20(l), 40(w)	32(l), 37(w)

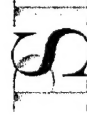


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# ***Option Program – Technical Objectives***

VG02-124-47

- **Synthesize and characterize self-doped polythiophene and polyaniline copolymers with desired properties**
- **Construct and characterize “dry” self-doped actuators**
  - Nafion or other appropriate electrolyte
  - Measure performance characteristics (speed, cycle operating lifetime, etc.) and compare to polyaniline or polythiophene baseline actuator
- **Perform detailed CD analysis on actuator materials to confirm polymer coiling, relate coiling to actuator performance**
- **(Investigate aqueous-based actuation with H<sub>2</sub>O-soluble EA polymers??)**



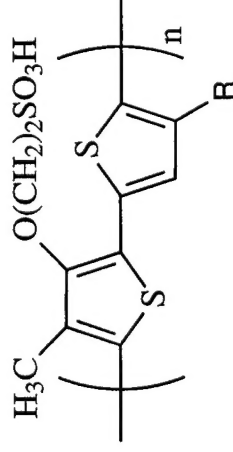
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# Candidate High-Conductivity Self-Doped EAPs

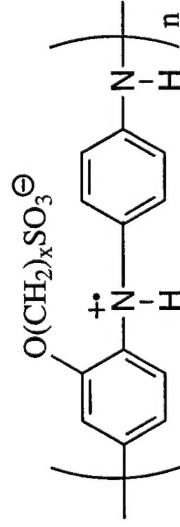
VG02-124-48

## Two synthetic strategies:

- Copolymerize self-doped monomer with hydrophobic monomer to achieve water-insolubility
- Synthesize amphiphilic bithiophene or bianiline monomer and polymerize



Bithiophene polymer (5-10 S/cm)



Aniline copolymer (30-40 S/cm)

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